Canadian Water Quality Guidelines for the Protection of Aquatic Life

MOLYBDENUM

Molybdenum (Mo) is a naturally occurring element that comprises approximately 0.0015% of the earth's crust (Chappell 1975). It can exist in the valence states +2 through +6 and occurs as mineral deposits mainly as molybdenite (MoS_2) and also as powellite ($CaOMo_3$) and wulfenite or lead molybdate ($PbMoO_4$). Molybdenum also occurs in minerals containing iron, bismuth, or copper and may be associated with coal or uranium deposits. Canadian production of molybdenum in 1993 was approximately 10 000 kg, accounting for 8.4% of the world's total production (NRC 1994). Currently, British Columbia is the only province where molybdenum is mined (Giancola 1994).

Molybdenum is a component in alloys used in filaments, X-ray tubes, screens, grids for radios, spark plugs, contacts, induction heating elements, and metal spray applications. Molybdenum compounds are present in lubricants, printing inks, lacquers, paints, rubbers, leathers, and fertilizers, and are also used extensively in the petroleum industry (Stokinger 1981).

Natural sources of molybdenum to the aquatic environment include the weathering of ores from igneous and sedimentary rock (especially shale) and subsequent runoff to streams and lakes. Molybdenum may also enter the aquatic environment through leaching processes near molybdenum mines and burning of fossil fuels (Phillips and Russo 1978). An important anthropogenic source of molybdenum to aquatic systems is the use of fertilizers containing molybdenum (McNeely et al. 1979). Atmospheric wet deposition is a relatively insignificant source of molybdenum to aquatic systems as the measured concentration in precipitation in urban areas is 0.2 $\mu g \cdot L^{-1}$ (Campbell et al. 1982; Galloway 1982).

Concentrations of molybdenum in Canadian freshwater sources range from below the limit of detection (0.1 $\mu g \cdot L^{-1}$) to 500 $\mu g \cdot L^{-1}$ (OMOEE 1995). In British Columbia, the only province where molybdenum is currently mined, the surface water concentrations range from below the limit of detection (0.1 $\mu g \cdot L^{-1}$) to 57 $\mu g \cdot L^{-1}$ for total molybdenum (A. Ryan 1998, British Columbia Ministry of the Environment, Vancouver, pers. com.) In areas associated with human and industrial activity, the surface water concentrations of molybdenum average 70 $\mu g \cdot L^{-1}$ (Chappell 1975). Concentrations in the Great Lakes range from 0.15 to 2.8 $\mu g \cdot L^{-1}$ (Rossmann and Barres 1988).

Chappell (1975) found that the level of molybdenum in aquatic sediments varied substantially, ranging from 2 to 400 $mg \cdot kg^{-1}$, while Webb et al. (1968) found that stream sediments contained an average concentration of 2 $mg \cdot kg^{-1}$.

Molybdenum readily forms organometallic complexes in aquatic systems (Cotton and Wilkinson 1980). The dominant forms in water are molybdenum sulphide (MoS_2), molybdate (MoO_4^{2-}), and bimolybdate ($HMoO_4^-$) (Jarrell et al. 1980). At pH >7, the molybdate anion predominates, whereas at pH <7, polymeric species tend to form. Adsorption, absorption, and co-precipitation with hydrous oxides of iron (Fe) and aluminum (Al) are processes that influence the fate of molybdenum in aquatic systems (Allaway 1977). Influenced by the pH, molybdenum will remain in solution at pH >5, and at pH <5 forms complexes with excess Fe and Al (LeGrande and Runnells 1975).

Molybdenum is an essential trace element and is, therefore, also found in aquatic organisms. It serves as a growth promoter for phytoplankton, periphyton, and macrophytes. Concentrations <0.06 $\mu g \cdot L^{-1}$ may be limiting, since lakes at these levels experience increased primary productivity when molybdenum is added. Optimal concentrations for growth appeared to be 25 $\mu g \cdot L^{-1}$, with inhibition occurring above this concentration (Dumont 1972; Eisler 1989).

Fish introduced to a creek near a molybdenum tailings pile had liver and kidney levels of 43 and 26 $mg \cdot kg^{-1}$ dw, respectively, compared to control concentrations of 1 and

Table 1. Water quality guidelines for molybdenum for the protection of aquatic life (Fletcher et al. 1997).

Aquatic life	Guideline value ($\mu g \cdot L^{-1}$)
Freshwater	73*
Marine	NRG†

*Interim guideline.

†No recommended guideline.

1.6 mg·kg^{-1} dw, respectively, after a 2-week exposure (Kienholz 1977). This suggests bioconcentration factors of <100. Rainbow trout *(Oncorhynchus mykiss)* collected from areas with molybdenum concentrations of 300 µg·L^{-1} had tissue concentrations less than 12-fold compared to areas with no molybdenum (Ward 1973). Fathead minnows *(Pimephales promelas)* and Colorado squawfish *(Ptychocheilus lucius)* exposed for 76 d to spent oil shale leachate containing high molybdenum concentrations and a mixture of metals showed only slightly increasing accumulation with increasing exposure concentration. BCFs were not much greater than 1 (Woodward et al. 1985). A study with lake trout *(Salvelinus namaycush)* aged 1 through 12 years showed that the highest concentrations of 8.2 and 8.5 µg·kg^{-1} fresh weight (fw) occurred in fish that were 1 and 2 years old (Tong et al. 1974). There was a gradual decrease to 2.2 and 2.8 µg·kg^{-1} fw in fish that were 11 and 12 years old. This evidence indicates a lack of bioaccumulation in fish.

Several species of aquatic insects concentrated molybdenum even at waterborne concentrations below the detection limit (1.0 µg·L^{-1}) (Colburn 1982). For the algal species *Scenedesmus chlorelloides* and *Chlamydomonas reinhardtii*, the calculated BCFs ranged from 756 to 2321 and from 944 to 2116, respectively (Sakaguchi et al. 1981). The macrophyte *Ranunculus aquatilis* concentrated radioactive molybdenum (^{99}Mo) about 300-fold in exposures up to 18 d (Svadlenkova et al. 1990).

Water Quality Guideline Derivation

The interim Canadian water quality guideline for molybdenum for the protection of freshwater life was developed based on the CCME protocol (CCME 1991). For more information, see the supporting document (Fletcher et al. 1997).

Freshwater Life

The acute toxicity values (96-h LC_{50}s) for vertebrates include values for fathead minnows *(P. promelas)* exposed to MoO_3 in soft (20 mg·L^{-1}) and hard (400 mg·L^{-1}) water of 70 and 370 mg·L^{-1}, respectively (Tarzwell and Henderson 1960). Kimball (n.d.) reported a value of 628 mg·L^{-1} for the same species. Rainbow trout (*O. mykiss*) exposed to sodium molybdate resulted in a 96-h LC_{50} value of 800 mg·L^{-1} (McConnell 1977).

For invertebrates, *Daphnia magna* neonates had 48-h LC_{50}s of >403 mg·L^{-1} with feeding and 206.8 mg·L^{-1} without feeding and a 96-h EC_{50} (immobilization) of 34.4 mg·L^{-1} (Kimball n.d.). The 24-, 48-, and 96-h EC_{50}s (immobilization) for *Tubifex tubifex* were 56, 52, and 29 mg·L^{-1}, respectively (Khangarot 1991).

Chronic studies for vertebrates include 28-d LC_{50} values for *O. mykiss* eyed eggs of 0.79 mg·L^{-1} (Birge et al. 1979) and 0.73 mg·L^{-1} (Birge 1978). The 7-d LC_{50}s for the embryo of the toad *Gastrophryne carolinensis* was 0.96 mg·L^{-1} and 60 mg·L^{-1} for goldfish embryos *(Carassius auratus)*, although the confidence limits for the goldfish value were large (7.9–92.2 mg·L^{-1}) (Birge 1978).

Chronic values for invertebrates include a decrease in the number of young per female of *D. magna* at 4.5 mg·L^{-1} after 7 d of exposure and a 28-d LC_{50} of 0.93 mg·L^{-1}, where the mean number of offspring per female declined at 1.15 mg·L^{-1} (Kimball n.d.). Naddy et al. (1995) calculated 8-d $IC_{12.5}$, IC_{25}, and IC_{50} (reproduction as number of young after three broods) concentrations of 34.0, 47.5, and 79.7 mg·L^{-1}, respectively, for *Ceriodaphnia dubia*.

The alga *Chlorella regularis* was exposed for 96-h to 0, 5, 10, 20, and 50 mg·L^{-1} of ammonium molybdate. Observations were made at 24, 48, and 96 h. There were no effects on growth at 20 mg·L^{-1}, but growth was significantly inhibited at 50 mg·L^{-1} in all exposure durations (Sakaguchi et al. 1981). The highest concentration tolerated for *C. vulgaris* was 10 mg·L^{-1}, and the

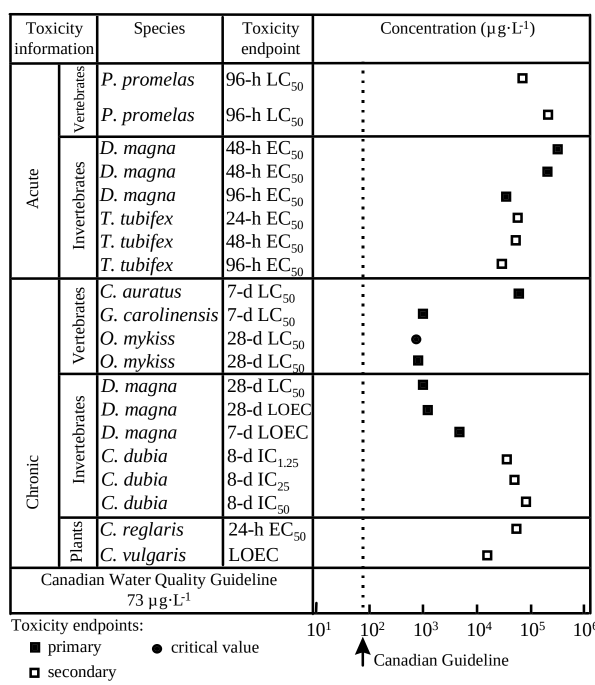

Figure 1. Select freshwater toxicity data for molybdenum.

lowest inhibitory concentration was 15 $mg \cdot L^{-1}$ for a chronic exposure of 3 to 4 months in growth media containing ammonium molybdate (Den Dooren De Jong 1965).

The interim water quality guideline for molybdenum for the protection of freshwater life is 73 $\mu g \cdot L^{-1}$ (Fletcher et al. 1997). It was derived by multiplying the lowest chronic toxicity value, the 28-d LC_{50} of 0.73 $mg \cdot L^{-1}$ for rainbow trout *(O. mykiss)* (Birge 1978), by a safety factor of 0.1 (CCME 1991).

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